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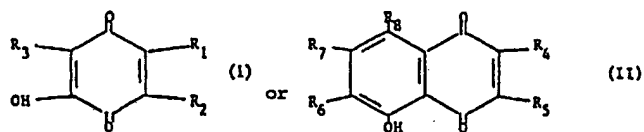
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(54) Dyeing hair with hydroxy-quinone dyes

(57) A process for dyeing human keratinous fibres which comprises applying to the fibres in separate stages in any order:

a composition (A) comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium; and

a composition (B) comprising, in a cosmetically acceptable medium, at least one dye of formula:



in which:

R₁ denotes hydrogen or hydroxy;

R₂ and R₃ independently denote hydrogen, alkyl or alkoxy;

R₄ denotes hydrogen, hydroxy, alkoxy, alkyl or chlorine;

R₅ denotes hydrogen, chlorine, alkoxy or hydroxy; and

R₆, R₇ and R₈ independently denote hydrogen or hydroxy.

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SPECIFICATION

A process for dying hair

5 The present invention relates to a process for dyeing hair, especially living human hair, with hydroxyquinone dyes. 5

Quinone dyes have been used for a long time for dyeing hair. For example lawsone, the dyeing principle of henna, was used by the ancient Egyptians.

French Patents 2,517,199, 2,517,200 and 2,537,433 describe the use of other hydroxy-naphthoquinones or hydroxybenzoquinones for the direct dyeing of hair. 10

In hair dyeing, a capacity for providing the widest possible range of coloration is generally sought to provide natural hues and hues having glints. As a result, the creation of new and powerful hues is in particular demand.

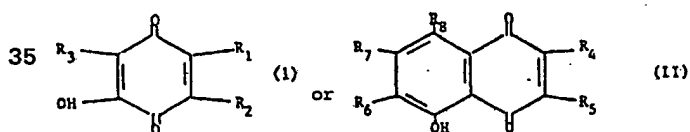
We have discovered that it is possible to improve substantially the tinctorial strength or colouring power of certain hydroxyquinone dyes by means of a pre- or post-treatment with a metal salt. 15

It is possible to obtain new colorations without a fall in strength by means of a pre- or post-treatment with a metal salt, these colorations being expressed in terms of a difference in hue according to Munsell's notation (ASTM Standard D1535 "Standard Method of Specific Color by the Munsell System") or in Munsell's Book of Color, 1966 Macbeth Color and Photometry Division Kollmorgen Corporation Newburgh, New York, USA. The colours are designated in Munsell's system by the formula HV/C, in which H denotes the hue, V the brightness or value and C the chrominance or "chroma". We have found that it is possible to obtain more intense colours, shown by a variation in H or V, When a pre- or post-treatment with a particular metal salt is used, compared with the same dye used without this pre- or post-treatment. 20 25

The tints thereby obtained possess, moreover, satisfactory light- and washing-fastness.

The present invention provides a process for dyeing human keratinous fibres, especially living human hair, which comprises applying to the fibres in separate stages in any order:

a composition (A) comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium; and 30
a composition (B) comprising, in a cosmetically acceptable medium, at least one dye of formula:



40 in which:

R₁ denotes hydrogen or hydroxy;

R₂ and R₃ independently denote hydrogen, alkyl or alkoxy;

R₄ denotes hydrogen, hydroxy, alkoxy, alkyl or chlorine;

R₅ denotes hydrogen, chlorine, alkoxy or hydroxy; and

45 R₆, R₇ and R₈ independently denote hydrogen or hydroxy. 45

The alkyl and alkoxy groups preferably contain 1 to 4 carbon atoms.

The preferred dyes are 3-methyl-2,5-dihydroxy-1,4-benzoquinone, 3-methyl-6-methoxy-2,5-dihydroxy-1,4-benzoquinone, 5-hydroxy-1,4-naphthoquinone, 2-methoxy-5-hydroxy-1,4-naphthoquinone and 2,5-dihydroxy-1,4-naphthoquinone.

50 The dye is preferably in composition (B) in a proportion of from 0.05 and 5% by weight relative to the total weight of the composition. 50

The metal salts are, in particular, salts of acids which are cosmetically acceptable, such as acetates, sulphates, lactates, glycinates, propionates, butyrates, nitrates or chlorides.

The most preferred salts are copper, cobalt, iron or silver salts, or a mixture thereof.

55 The content of metal produced from the metal salt in composition (A) is preferably from 0.01 to 2% by weight relative to the total weight of the composition, preferably from 0.1 to 1%. 55

Each composition is generally an aqueous composition which may contain ingredients which are customarily used in cosmetic compositions for dyeing hair, such as solvents, surfactants, thickeners, treatment agents, alkalizing or acidifying agents for adjusting the pH, preservatives or perfumes. 60

Composition (A) is preferably in the form of a solution having a pH of from 3 to 11.

Composition (B) is preferably in the form of a solution thickened to a greater or lesser extent, an emulsion (such as, for example, a cream), a gel, an aerosol foam or any other form suitable for dyeing hair. This composition preferably has a pH of from 3 to 11.

65 The alkalizing agent is generally an alkanolamine or alkali metal or ammonium hydroxide or 65

carbonate. The acidifying agent is preferably an organic or inorganic acid such as lactic acid, acetic acid, tartaric acid, citric acid, phosphoric acid or hydrochloric acid.

The solvent is generally a cosmetically acceptable organic solvent, more especially an alcohol such as ethyl alcohol, isopropyl alcohol, benzyl alcohol or phenylethyl alcohol, a glycol or glycol ether such as ethylene glycol, and its monomethyl, monoethyl or monobutyl ethers, propylene glycol, butylene glycol or dipropylene glycol, or an alkyl ether such as diethylene glycol monobutyl ether. The solvent is preferably present in an amount of from 0.5 to 75%, preferably from 2 to 50%, by weight relative to the total weight of each of the compositions. 5

The surfactant may be an anionic, cationic, nonionic or amphoteric surfactant, or a mixture thereof. The surfactant is preferably present in a proportion of from 0.1 to 50% by weight, and advantageously from 1 to 20% by weight, relative to the total weight of the composition. 10
Examples of surfactants are anionic agents such as alkali metal salts, magnesium salts, ammonium salts, amine salts and alkanolamine salts of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamide sulphates ethoxylated or otherwise, alkylamide sulphates, alpha-olefin sulphonates or alkyl sulphaacetates; the alkyl radicals in these compounds having 12 to 18 15 carbon atoms.

It is possible to use the abovementioned salts of fatty acids such as lauric, myristic, oleic, ricinoleic, palmitic or stearic acids, hydrogenated coconut oil acids or polyglycol ether carboxylic acids.

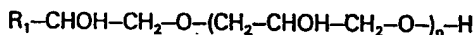
20 Examples of cationic surfactants are fatty amine salts, quaternary ammonium salts such as alkyldimethylbenzylammonium or dimethyldialkylammonium chlorides or bromides, alkylpyridinium salts or imidazoline derivatives. The alkyl groups in the quaternary ammonium derivatives are long-chained groups preferably having from 12 to 18 carbon atoms. 20

An example of a cationic surfactant is an amine oxide.

25 Examples of amphoteric surfactants are alkylamino(mono- and di)propionates, betaines such as alkylbetaines, N-alkylsulphobetaines or N-alkylaminobetaines, the alkyl radical having from 8 to 22 carbon atoms, or cycloimidinium compounds such as alkylimidazolines. 25

Preferred nonionic surfactants are

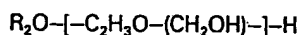
a) the products of the condensation of monohydric alcohol, an α -diol, an alkylphenol or an amide with glycidol or a glycidol precursor, in particular of formula: 30



in which R_1 denotes an aliphatic, cycloaliphatic or arylaliphatic radical, preferably having from 7 to 21 carbon atoms, or a mixture thereof, the aliphatic chains optionally containing at least one ether, thioether or hydroxymethylene group, and p has a value of from 1 to 10. 35

Especially preferred compounds are those in which R_1 denotes a mixture of alkyl radicals having from 9 to 12 carbon atoms and p has a statistical value of 3.5, or alternatively those in which R_1 denotes a C_{10} alkyl radical and p has a statistical value of 2.5. Such compounds are 40 described, in particular, in French Patent No. 2,091,516. 40

b) products of formula:



in which R_2 denotes an alkyl, alkenyl or alkylaryl radical and q has a statistical value of from 1 to 10. The preferred compounds are those in which R_2 denotes a $C_{12}H_{25}$ group and q has a statistical value of 4 to 5. These compounds are described, in particular, in French Patent 1,477,048. 45

c) products of formula:

50 $R_3CONH-CH_2-CH_2-O-CH_2-CH_2-O-(CH_2CHOH-CH_2-O)_r-H$ 50

in which R_3 denotes a saturated or unsaturated, linear or branched aliphatic radical, or mixture thereof, optionally containing one or more hydroxyl groups, and having from 8 to 30 carbon atoms, of natural or synthetic origin, and r has a value of from 1 to 5 and represents the average degree of condensation; the especially preferred compounds are these in which R_3 denotes a mixture of radicals derived from lauric, myristic, oleic or coconut acids and r has a statistical value of 3 to 4. Such compounds are described, more especially in French Patent 2,328,763. 55

60 d) polyethoxylated or polyglycerolated alcohols, alkylphenols or fatty acids having a C_8 to C_{18} fatty chain, condensates of ethylene oxide and propylene oxide with fatty alcohols, polyethoxylated fatty amides containing at least 5 moles of ethylene oxide per mole of fatty amide, and polyethoxylated fatty amines. 60

The composition may also, for example, contain amides such as the mono- and diethanolamides of fatty acids derived from coconut, of lauric acid or of oleic acid, preferably in a concentration of 5 to 10%. 65

tion of from 0.05 to 10% by weight relative to the total weight of the composition.

The thickening agents are preferably sodium alginate, gum arabic, xanthan gum, guar gum, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose or the sodium salt of carboxymethylcellulose, or acrylic acid polymers. It is also possible to use inorganic thickening agents such as bentonite. These thickeners are used alone or mixed, and are preferably present in a proportion of from 0.1 to 5% by weight relative to the total weight of each of the compositions, advantageously from 0.2 to 3% by weight.

The composition can contain other dyes, for example direct dyes, apart from those of formula (I) or (II), for example a nitro derivative of the benzene series, anthraquinone, azo or natural dyes. Composition (B), for example in aqueous form, may be prepared at the time of use from a composition comprising the dye of formula (I) or (II) in anhydrous form, in the presence of an organic solvent such as defined above, the composition containing less than 1% water by weight. This is especially advantageous when the dye is unstable in an aqueous medium.

The anhydrous composition can contain, in addition, an anhydrous nonionic surfactant as described in French Patent Application No. 83/07,045.

Composition (B) can also be prepared from a mixture of powders comprising the dye of formula (I) or (II), or a powdered product containing it, and a flour, a starchy or mucilaginous substance, a silica, a powdered plant, a clay or a plant powdered after extraction of an active principle. This product is diluted with water, a solvent or an oil which is cosmetically acceptable, to provide a product, known as a "cataplasm", having a viscosity of 0.1 to 9 Pa.s. Composition (A) is preferably applied to the hair before the application of the cataplasm.

The process of the present invention is preferably carried out by applying to human keratinous fibres, in separate stages, composition (A) having a pH of from 3 to 11 for from 3 to 30 minutes, more especially from 5 to 10 minutes, and composition (B) for from 3 to 40 minutes, preferably from 5 to 30 minutes, the hair then preferably being rinsed, optionally washed and dried.

Composition (A) is applied either before or after composition (B), the hair being rinsed between the two applications.

The present invention also provides a multi-compartment device or kit for dyeing human keratinous fibres which comprises, in a first compartment, a composition comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium, and, in a second compartment, a composition comprising at least one dye of formula (I) or (II) as defined above, in a cosmetically acceptable medium.

A third compartment can be provided when the composition containing the dye is anhydrous, the latter compartment containing an aqueous cosmetic vehicle.

The present invention further provides a multi-compartment device or kit for dyeing human keratinous fibres which comprises, in a first compartment, a composition comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium, in a second compartment, an anhydrous composition comprising at least one dye of formula (I) or (II) as defined above, in a cosmetically acceptable solvent, and in a third compartment, a composition comprising at least one of solvent, surfactant, thickener, treatment agent, alkalizing or acidifying agent, preservative or perfume, in a cosmetically acceptable aqueous medium.

The Examples which follow further illustrate the invention.

EXAMPLE 1

The following compositions are prepared:

COMPOSITION A

50	CuSO ₄ .5H ₂ O		1	g	50
	Monoethanolamine	qs pH 9.3			
	Water	qs	100	g	

COMPOSITION B

55	2,5-Dihydroxy-3-methyl-1,4-benzoquinone		0.5	g	55
	Butyldiglycol		50	g	
	Sodium carbonate	qs pH 3			
	Water	qs	100	g	

60 The composition A is applied for 5 minutes on hair which is 90% white; it is rinsed and the composition B is applied and left in place for 30 minutes. After rinsing, a partly golden brown hue is obtained.

This composition can be packaged in a dyeing kit incorporating two compartments which contain the compositions A and B, respectively.

EXAMPLE 2

The following compositions are prepared:

COMPOSITION A

5	CuSO ₄ ·5H ₂ O	0.5 g	5
	Sodium alkyl ether sulphate, 0.6 meq/g	5 g	
	Xanthan gum sold under the name "RHODOPOL 23 SC" by RHONE-POULENC	0.32 g	
	NH ₄ OH	qs pH 10.8	
10	Water	qsp 100 g	10

COMPOSITION B

	2,5-Dihydroxy-1,4-naphthoquinone	0.2 g	
	2-Methoxy-5-hydroxy-1,4-naphthoquinone	0.15 g	
15	Nonylphenol oxyethyleneated with 9 moles of ethylene oxide	10 g	15
	Butyldiglycol	50 g	
	Ethyl alcohol	10 g	
	Monoethanolamine	qs pH 5	
20	Water	qs 100 g	20

The composition A is applied for 10 minutes on hair which is 90% white. It is rinsed and the dyeing composition B is applied and left in place for 20 minutes. After rinsing, a pearly beige blond coloration is obtained.

25 Table I to IV below illustrate the use of aqueous dyeing compositions (B). 25

Examples 3 and 6 to 15 inclusive illustrate a post-treatment with a metal salt, that is to say, in these examples, the composition B is applied on the hair for 30 minutes, the hair is rinsed and the composition A is applied and left in place for 5 minutes. After rinsing, the indicated hue is obtained.

30 Examples 4 and 5 and 16 to 28 inclusive illustrate a pretreatment with a metal salt, that is to say, in these examples, the composition A is applied for 5 minutes; the hair is rinsed and the composition B is applied and left in place for 30 minutes. After rinsing, the indicated hue is obtained. 30

TABLE I

5	Example No.	3	4	5	6	7	8	9	5
	<u>Composition A</u>								
10	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$				1 g		1 g	1 g	10
	$\text{Cu}(\text{NO}_3)_2$	1 g	1 g			1 g			
15	Cupric acetate			1 g					15
	Monoethanolamine qs pH:	9		9	9	9		9	
	Lactic acid qs pH:		4				4		
20	Water qs g	100	100	100	100	100	100	100	20
25	<u>Composition B</u>								25
	2,5-Dihydroxynaph-								
30	thoquinone	0.5 g	0.5 g	0.5 g					30
	3-Methyl-6-methoxy-								
35	2,5-dihydroxybenzo-								35
	quinone				0.5 g	0.5 g	0.5 g	0.5 g	
	Butyldiglycol	50 g	50 g	50 g	50 g	50 g	50 g	50 g	
40	Monoethanolamine								40
	qs pH:	9	9	9					
45	Lactic acid qs pH:				4	4	4	4	45
	Water qs g	100	100	100	100	100	100	100	
50	Coloration obtained on 90% white natural hair				pale olive- grey	pale olive- grey			50
55	On 90% white perma- nent-waved hair	grey- ish red- brown	pale brown	me- dium red- brown			dark yellow	greyish olive	55

TABLE II

5	Example No.	10	11	12	13	14	15	16	5
	<u>Composition A</u>								
10	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$							1 g	10
	CuCl_2			1 g	1 g				
	$\text{Cu}(\text{NO}_3)_2$	1 g	1 g						
15	Cupric acetate					1 g	1 g		15
	Monoethanolamine qs pH:		9		9		9		
20	Lactic acid qs pH:	4		4		4		4	20
	Water qs g	100	100	100	100	100	100	100	
25	<u>Composition B</u>								25
	3-Methyl-6-methoxy-								
30	2,5-dihydroxybenzo-								30
	quinone	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	
35	Butyldiglycol	50 g	50 g	50 g	50 g	50 g	50 g	50 g	35
	Lactic acid qs pH:	4	4	4	4	4	4	4	
40	Water qs g	100	100	100	100	100	100	100	40
	Coloration obtained	me-	grey-	me-	olive-	pale	olive-	medium	
	on 90% white	dium	ish	dium	grey	olive-	grey	olive	
45	permanent-waved hair	olive	olive	olive		brown			45

TABLE III

5	Example No.	17	18	19	20	21	22	5
	<u>Composition A</u>							
10	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1 g						10
	CuCl_2				1 g	1 g		
	$\text{Cu}(\text{NO}_3)_2$		1 g	1 g				
15	Cupric acetate						1 g	15
	Monoethanolamine qs pH:	9		9		9		
20	Lactic acid qs pH:		4		4		4	20
	Water qs g	100	100	100	100	100	100	
25	<u>Composition B</u>							25
	3-Methyl-6-methoxy- 2,5-dihydroxybenzo-							
30	quinone	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	30
35	Butyldiglycol	50 g	50 g	50 g	50 g	50 g	50 g	35
	Lactic acid qs pH:	4	4	4	4	4	4	
40	Water qs g	100	100	100	100	100	100	40
	Coloration obtained on 90% white permanent-waved hair	pale olive	pale olive- brown	medium olive	medium olive	medium olive	medium olive- brown	45

TABLE IV

5	Example No.	23	24	25	26	27	28	5
	<u>Composition A</u>							
10	Cupric acetate	1 g						10
	CoCl ₂		1 g					
	Mg acetate			1 g				
15	FeCl ₂					1 g	1 g	15
	AgNO ₃				1 g			
20	Monoethanolamine qs pH: 9							20
	Lactic acid qs pH:		4	4	4	4	4	
25	Water qs g	100	100	100	100	100	100	25
	<u>Composition B</u>							
30	3-Methyl-6-methoxy- 2,5-dihydroxybenzo-							30
35	quinone	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	35
	Butyldiglycol	50 g	50 g	50 g	50 g	50 g	50 g	
40	Monoethanolamine qs pH:						9	40
	Lactic acid qs pH:	4	4	4	4	4		
45	Water qs g	100	100	100	100	100	100	45
	Coloration obtained on 90% white permanent-waved hair	medium olive	medium yellow- brown	grey yellow- brown	pale olive- brown	dark red	medium yellow- brown	
50								50

Tables V and VI below illustrate the use of dyes in an anhydrous medium.

In Examples Nos. 29 to 43, the composition (A) is applied for 5 minutes on the hair; it is rinsed and the composition B, diluted with water in the ratio 1:1.5 by weight, is applied. It is left in place for 30 minutes and the hair is rinsed.

TABLE V

Example No.	29	30	31	32	33	34	35	36	
5									5
<u>Composition A</u>									
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1 g			1 g	1 g				
10 CuCl_2		1 g						1 g	10
$\text{Cu}(\text{NO}_3)_2$						1 g	1 g		
15 AgNO_3			1 g						15
Monoethanolamine qs pH:	9	9			9		9		
20 Lactic acid qs pH:			4	4		4		4	20
Water qs g	100	100	100	100	100	100	100	100	
25									25
<u>Composition B</u>									
30 2,5-Dihydroxynaphthoquinone	1.25g	1.25g	1.25g						30
3-Methyl-6-methoxy-2,5-dihydroxybenzoquinone				1.25g	1.25g	1.25g	1.25g	1.25g	
35 Ethanolamine derivative (AMIELTOL M 21)	1 g	1 g	1 g						35
Lactic acid				1 g	1 g	1 g	1 g	1 g	
40 Ethyl alcohol g	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	40
Nonylphenol oxyethyleneated with 9 moles of ethylene oxide, qs g.	100	100	100	100	100	100	100	100	45
45 Coloration obtained on 90% white natural hair	grey-brown	pale brown	medium brown						
50 On 90% white permanent-waved hair				dark grey-brown	medium olive	medium olive-brown	medium olive	medium olive-brown	50

TABLE VI

Example No.	37	38	39	40	41	42	43
5 <u>Composition A</u>							
CuCl_2	1 g						
10 Cupric acetate		1 g	1 g				
CoCl_2				1 g			
Mg acetate					1 g		
15 FeCl_2						1 g	
AgNO_3							1 g
20 Monoethanolamine qs pH:	9		9				
Lactic acid qs pH:		4		4	4	4	4
25 Water qs g	100	100	100	100	100	100	100
30 <u>Composition B</u>							
3-Methyl-6-methoxy-2,5-dihydroxybenzoquinone g	1.25	1.25	1.25	1.25	1.25	1.25	1.25
35 Amietol M 21							1 g
Lactic acid	1 g	1 g	1 g	1 g	1 g	1 g	
40 Ethyl alcohol g	28.5	28.5	28.5	28.5	28.5	28.5	28.5
Nonylphenol oxyethyleneated with 9 moles of ethylene oxide, qs g	100	100	100	100	100	100	100
45 Coloration obtained on 90% white natural hair							medium red-brown
50 On 90% white permanent-waved hair	medium olive	medium olive-brown	medium olive	grey red-brown	dark grey-violet	dark grey-brown	

55

55

Tables VII and VIII below illustrate the use of a colouring cataplasma.

In Examples 44 to 57, the composition (A) is applied for 5 minutes on the hair; it is rinsed and the composition (B), diluted with water in the ratio 1:3 by weight, is applied. It is left in place for 30 minutes and the hair is rinsed.

TABLE VII

Example No.	44	45	46	47	48	49	50	
5								5
Composition A								
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1 g	1 g						
10 CuCl_2					1 g	1 g		10
$\text{Cu}(\text{NO}_3)_2$			1 g	1 g				
Cupric acetate							1 g	15
Monoethanolamine qs pH:		9		9		9		
Lactic acid qs pH:	4		4		4		4	
20 Water qs g	100	100	100	100	100	100	100	20
25								25
Composition B								
3-Methyl-6-methoxy-2,5-dihydroxybenzoquinone	2 g	2 g	2 g	2 g	2 g	2 g	2 g	
30 Powdered residues of exhaustive extraction of Saponaria, of particle size $< 80 \mu\text{m}$	35 g	35 g	35 g	35 g	35 g	35 g	35 g	30
35 Maize cobs	15 g	15 g	15 g	15 g	15 g	15 g	15 g	35
Lactic acid	4 g	4 g	4 g	4 g	4 g	4 g	4 g	
40 Carob gum sold under the name "VIDOGUM L 175" by UNIPLECTINE	3 g	3 g	3 g	3 g	3 g	3 g	3 g	40
45 Fat-free soluble powdered milk qs g	100	100	100	100	100	100	100	45
Coloration obtained on 90% white permanent-waved hair	medium olive brown	medium olive	grey yellow brown	medium olive	medium olive	medium olive	medium olive-brown	50

TABLE VIII

Example No.	51	52	53	54	55	56	57	
5 <u>Composition A</u>								5
CuCl_2						1 g		
10 FeCl_2							1 g	10
Cupric acetate	1 g							
15 CoCl_2		1 g						15
Mg acetate			1 g					
AgNO_3				1 g	1 g			
20 Monoethanolamine qs pH:	9					9		20
Lactic acid qs pH:		4	4	4	4		4	
25 Water qs g	100	100	100	100	100	100	100	25
<u>Composition B</u>								
30 2,5-Dihydroxynaphthoquinone						2 g	2 g	30
3-Methyl-6-methoxy-2,5-dihydroxybenzoquinone	2 g	2 g	2 g	2 g	2 g			
35 Powdered residues of exhaustive extraction of Saponaria, of particle size $<80 \mu\text{m}$	35 g	35 g	35 g	35 g	30 g	30 g	30 g	35
40 Maize cobs	15 g	15 g	15 g	15 g	50 g	50 g	50 g	40
Lactic acid	4 g	4 g	4 g	4 g				
45 Anhydrous pure Na_2CO_3					3 g	3 g	3 g	45
Carob gum sold under the name "VIDOGUM L 175" by UNIPLECTINE	3 g	3 g	3 g	3 g				
50 Fat-free soluble powdered milk qs g	100	100	100	100	100	100	100	50
Coloration obtained on 90% white natural hair						medium red-brown		
55 90% white permanent-waved hair	medium olive	medium brown	grey-violet	grey red-brown	grey red-brown		dark red-brown	55

EXAMPLE 58**Composition A**CuSO₄.5H₂O

Monoethanolamine qs

5 Water qs

1 g

pH 9.3

100 g

5

Composition B

5-Hydroxy-1,4-naphthoquinone

Butyldiglycol

10 Water qs

pH 5.1

0.5 g

50 g

100 g

10

Composition (A) is applied for 5 minutes on natural 90% white hair; it is rinsed and the composition (B) is applied for 30 minutes. After rinsing, the hair is coloured chestnut-brown.

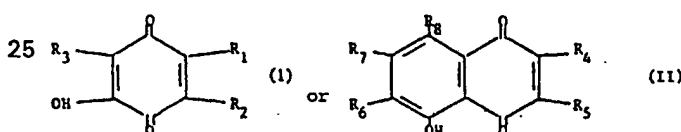
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CLAIMS

1. A process for dyeing human keratinous fibres which comprises applying to the fibres in separate stages in any order:

20 a composition (A) comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium; and

a composition (B) comprising, in a cosmetically acceptable medium, at least one dye of formula:



25

30 in which:

R₁ denotes hydrogen or hydroxy;

R₂ and R₃ independently denote hydrogen, alkyl or alkoxy;

R₄ denotes hydrogen, hydroxy, alkoxy, alkyl or chlorine;

R₅ denotes hydrogen, chlorine, alkoxy or hydroxy; and

35 R₆, R₇ and R₈ independently denote hydrogen or hydroxy.

35

2. A process according to claim 1, wherein the dye is 3-methyl-2,5-dihydroxy-1,4-benzoquinone, 3-methyl-6-methoxy-2,5-dihydroxy-1,4-benzoquinone, 5-hydroxy-1,4-naphthoquinone, 2-methoxy-5-hydroxy-1,4-naphthoquinone or 2,5-dihydroxy-1,4-naphthoquinone.

3. A process according to claim 1 or 2 wherein the metal salt is present in composition (A) in an amount of 0.01 to 2% by weight of metal relative to the total weight of the composition.

40

4. A process according to any one of claims 1 to 3 wherein the dye is present in composition (B) in a proportion of from 0.05 to 5% by weight relative to the total weight of the composition.

5. A process according to any one of claims 1 to 4 wherein composition (A) has a pH of from 3 to 11 and is applied to the fibres for from 3 to 30 minutes, and composition (B) has a pH of from 3 to 11 and is applied to the fibres for from 3 to 40 minutes, the fibres being rinsed between the two applications.

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6. A process according to any one of claims 1 to 5 wherein each composition is in the form of a liquid thickened to a greater or lesser extent, a gel, an emulsion, an aerosol foam or is prepared by diluting a mixture of powders shortly before use.

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7. A process according to any one of claims 1 to 6 wherein each composition is in aqueous form comprising at least one cosmetically acceptable ingredient which is a solvent, surfactant, thickener, treatment agent, alkalizing or acidifying agent, preservative or perfume.

8. A process according to claim 7 wherein the solvent comprises an alcohol, glycol, glycol ether or alkyl ether which is present in a proportion of from 0.5 to 75% by weight relative to the total weight of each composition.

55

9. A process according to any one of claims 1 to 8 wherein each composition comprises at least one anionic, cationic, nonionic or amphoteric surfactant, or a mixture thereof, in a proportion of from 0.1 to 50% by weight relative to the total weight of each composition.

60 10. A process according to any one of claims 1 to 9 wherein at least one composition comprises a fatty acid amide in a proportion of from 0.05 to 10% by weight relative to the total weight of the composition.

60

11. A process according to any one of claims 1 to 10 wherein at least one composition comprises a thickening agent in a proportion of from 0.1 to 5% by weight relative to the total weight of the composition.

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12. A process according to any one of claims 1 to 11 wherein composition (B) comprises a further dye, apart from that of formula (I) or (II) which is a nitro derivative of the benzene series, anthraquinone, azo or natural dye.

13. A process according to any one of claims 1 to 11 wherein composition (B) is prepared
5 by mixing immediately before use an anhydrous composition comprising at least one dye of formula (I) or (II) in a cosmetically acceptable solvent with a cosmetically acceptable aqueous medium as defined in any one of claims 7 to 11. 5

14. A process according to any one of claims 1 to 13 wherein, in a first stage, composition (A) is applied to the fibres and, in a second stage, a composition having a viscosity of from 0.1
10 to 9 Pa.s, resulting from the dilution with water, a cosmetically acceptable solvent or an oil, of a powder comprising at least one dye of formula (I) or (II) and a flour, a starchy or mucilaginous substance, a silica, a plant powdered after extraction of an active principle, a clay or a powdered plant, is applied to the fibres. 10

15. A process for dyeing human keratinous fibres substantially as hereinbefore described in
15 any one of the Examples. 15

16. A multi-compartment device or kit for dyeing human keratinous fibres which comprises, in a first compartment, a composition comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium, and, in a second compartment, a composition comprising at least one dye of formula (I) or (II) as defined
20 in claim 1, in a cosmetically acceptable medium. 20

17. A multi-compartment device or kit for dyeing human keratinous fibres which comprises, in a first compartment, a composition comprising a metal salt which is a copper, iron, cobalt, magnesium or silver salt, or a mixture thereof, in a cosmetically acceptable medium, in a second compartment, an anhydrous composition comprising at least one dye of formula (I) or (II) as
25 defined in claim 1, in a cosmetically acceptable solvent, and in a third compartment, a composition comprising at least one of solvent, surfactant, thickener, treatment agent, alkalinizing or acidifying agent, preservative or perfume, in a cosmetically acceptable aqueous medium. 25

18. A multi-compartment device or kit for dyeing human keratinous fibres according to claim
30 16 or 17 wherein the compositions contained therein are substantially as hereinbefore described in any one of Examples. 30